Morphology and properties of thermoset blends made from unsaturated polyester resin, poly(vinyl acetate) and styrene

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Blends containing an unsaturated polyester resin, poly(vinyl acetate) (PVAc) and styrene monomer in various proportions were cured using benzoyl peroxide as initiator. The morphology of the cured blends was studied using scanning electron microscopy. Polyester resin formed the matrix at low PVAc concentrations and at low styrene contents. A co-continuous phase morphology was observed in blends containing PVAc concentrations $\geqslant 6\%$ and styrene levels $\geqslant 40\%$. Increasing the styrene content over the range 20% to 80% caused a narrowing of the principal dynamic loss peak, and an increase in peak height: peak temperature reached a maximum at 40% styrene. The change from particulate PVAc to co-continuous structure was associated with a sharp drop in G_{Ic} and K_{Ic}. Parallel studies have shown this transition to be important in 'low-profile' behaviour.

(Keywords: polyester resin; poly(vinyl acetate); co-continuous structure; phase separation; G_{Ic})

INTRODUCTION

Blending of styrenated polyester resins with modified poly(vinyl acetate) (PVAc) is standard commercial practice. Modified PVAc is an example of a 'low-profile' additive, which reduces or eliminates the surface irregularities that occur on curing sheet moulding compounds (SMCs) or dough moulding compounds (DMCs) based on polyester resins[1].

A previous paper from this laboratory[2] describes phase separation in blends containing one such additive: Union Carbide LP40A, a solution of acrylic-modified PVAc in styrene monomer. As the concentration of modified PVAc is raised from 8% to 16% in blends with styrenated polyester resin, the morphology changes from a dispersion of PVAc particles in a resin matrix to a co-continuous phase structure.

A limitation in working with this type of commercial modifier is that increasing the modifier content increases the styrene/polyester ratio as well as the PVAc concentration. This problem can be overcome by using plain PVAc to make a model system, but it must be recognized that the absence of terminal acrylic acid groups on the PVAc, and differences in molecular-weight distribution between the two types of polymer, will inevitably alter the solubility characteristics of the additive. The present paper considers the effects of independent variations in polyester, PVAc and styrene concentrations upon the morphology and mechanical properties of cured blends.

EXPERIMENTAL

The unsaturated polyester resin used in this programme was a Scott Bader product, based on 1 mol maleic anhydride, 1 mol isophthalic acid, 1 mol propylene glycol and 1 mol diethylene glycol. The thermoplastic additive was unmodified PVAc of $M_w = 190\,000$, supplied by BDH Ltd. Blends were made by dissolving the PVAc in styrene monomer at 60°C, and then adding the resin with manual stirring. At this stage all of the blends appeared transparent. After cooling to room temperature, and addition of 0.65% benzoyl peroxide, the solution was degassed and poured into a glass plate mould with 3 mm spacers. The blend was then cured at 120°C in an air circulating oven for 4 h.

Two series of blends were prepared. In the first series, the PVAc concentration was held constant at 6.0 wt%, and the amount of styrene in the blends was varied from 20% to 80% in steps of 10%. *Table 1* shows the resulting variation in the mole ratio of styrene monomer to resin double bonds, which are provided by the maleic anhydride. Some turbidity developed in blends containing low styrene concentrations, on standing at room temperature. In the second series, the styrene/polyester ratio was kept constant at 40/60, and the PVAc concentration was varied from 1% to 10%. The benzoyl peroxide level was 0.65% in all blends.

Scanning electron microscopy studies were carried out on Au/Pd coated fracture surfaces obtained from fracture mechanics tests. Dynamic mechanical measurements were made between −10 and 190°C at 10 Hz, using a Polymer Laboratories DMTA machine. Young's modulus was determined at 20°C in 100 s precision creep tests. Fracture mechanics tests were carried out at 23°C on sharply notched three-point bend specimens measuring $60 \times 12 \times 3\ \text{mm}^3$ with a span of 48 mm and a notch depth of 6 mm; the crosshead speed was $1.25\ \text{mm min}^{-1}$.

RESULTS

Electron microscopy

The effects of varying styrene content on morphology in blends containing 6% PVAc are illustrated in *Figure*

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Table 1 Compositions of blends in series 1 (all blends contain 6% PVAc, 0.65% benzoyl peroxide and 0.65% of an inert carrier for the peroxide)

Styrene (wt%)	20	30	40	50	60	70	80
Polyester (wt%)	73	63	53	43	33	23	13
Moles styrene / Moles maleic anh.	0.90	1.57	2.49	3.83	5.99	10.0	20.3

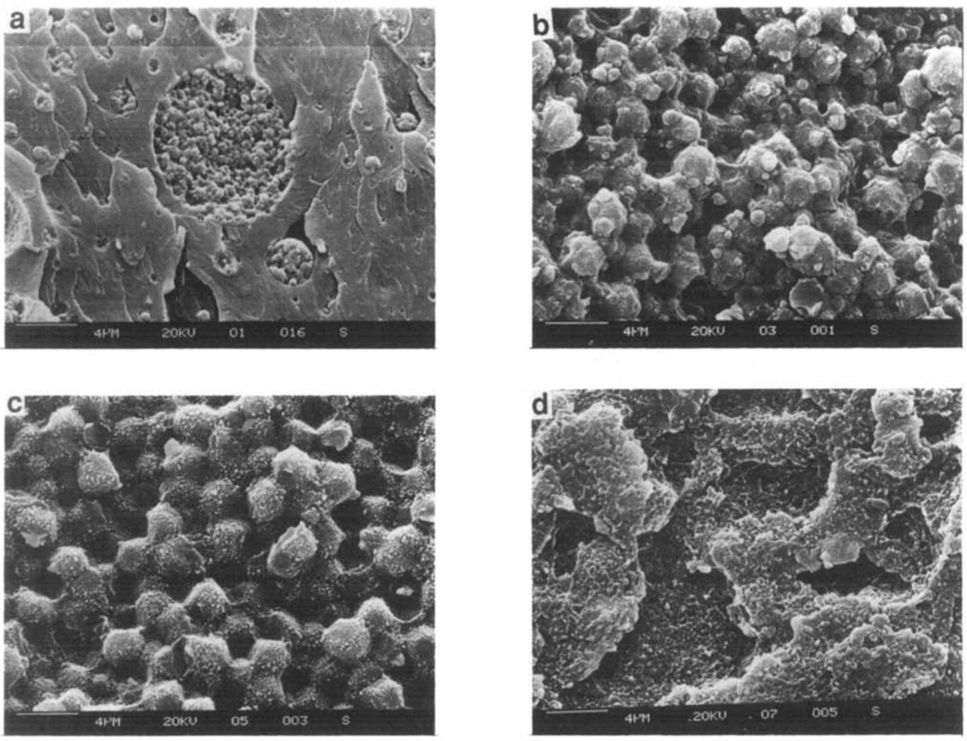

Figure 1 Scanning electron micrographs of fracture surfaces prepared at 23°C from blends containing 6% PVAc and various concentrations of styrene monomer: (a) 20%, (b) 40%, (c) 60% and (d) 80%

1. In order to identify the phases, selected specimens were etched with methyl ethyl ketone (MEK), which is a solvent for PVAc but has no effect on the crosslinked resin. However, all micrographs in the present paper were obtained from unetched fracture surfaces. At 20% styrene, the polyester resin forms a continuous matrix, and the PVAc forms spherical particles up to about 10 μm in diameter. The particles are composite in character: embedded in the PVAc phase are numerous spherical sub-inclusions of resin with diameters of ≈ 0.5 μm. This structure is similar to that reported previously[2], but with a wider spread of PVAc particle sizes.

Increasing the styrene content to 40% causes a marked change in morphology. The structure becomes co-continuous, with the resin precipitating as contiguous nodules between 1 and 3 μm in diameter. The PVAc-rich phase fills the remaining space. At 60% styrene, the morphology is similar, but the nodules are more uniform in size. Finally, in the blend containing 80% styrene and 13% polyester, there is insufficient resin to form a continuous phase, and the fracture surface shows a fine particulate structure, with a pattern of closely spaced particles about 0.5 μm in diameter embedded in a polystyrene-rich matrix.

The effects of varying PVAc concentration at a 40/60 styrene/polyester weight ratio are shown in *Figure 2*. Each micrograph is representative of the morphology of the blend. At the 1% level, PVAc forms discrete particles with diameters up to 0.5 μm. On close examination, one or two of these show evidence of sub-inclusions. Increasing the PVAc concentration to 3% causes a substantial increase in particle size, and the development of composite particles of the type described above, with numerous resin sub-inclusions. The result is a large increase in the effective volume fraction of the PVAc additive. At 4% PVAc, the structure becomes distinctly inhomogeneous. Large areas, consisting mainly of resin, alternate on a scale of about 100 μm with regions having a nodular co-continuous structure. The resin-rich areas contain small PVAc particles, and resemble *Figure 2a* in appearance; the nodule size in the co-continuous regions is about 4 μm. At 6% PVAc, only the nodular morphology is formed. Further increases in PVAc concentration between 6% and 10% produce little further change in structure.

Dynamic mechanical properties

Dynamic mechanical measurements at 10 Hz are presented in *Figure 3*. They show a major peak in tan δ for each of the blends, with a maximum in the range 100 to 115°C. Increasing the styrene concentration at fixed PVAc content causes this principal peak to become

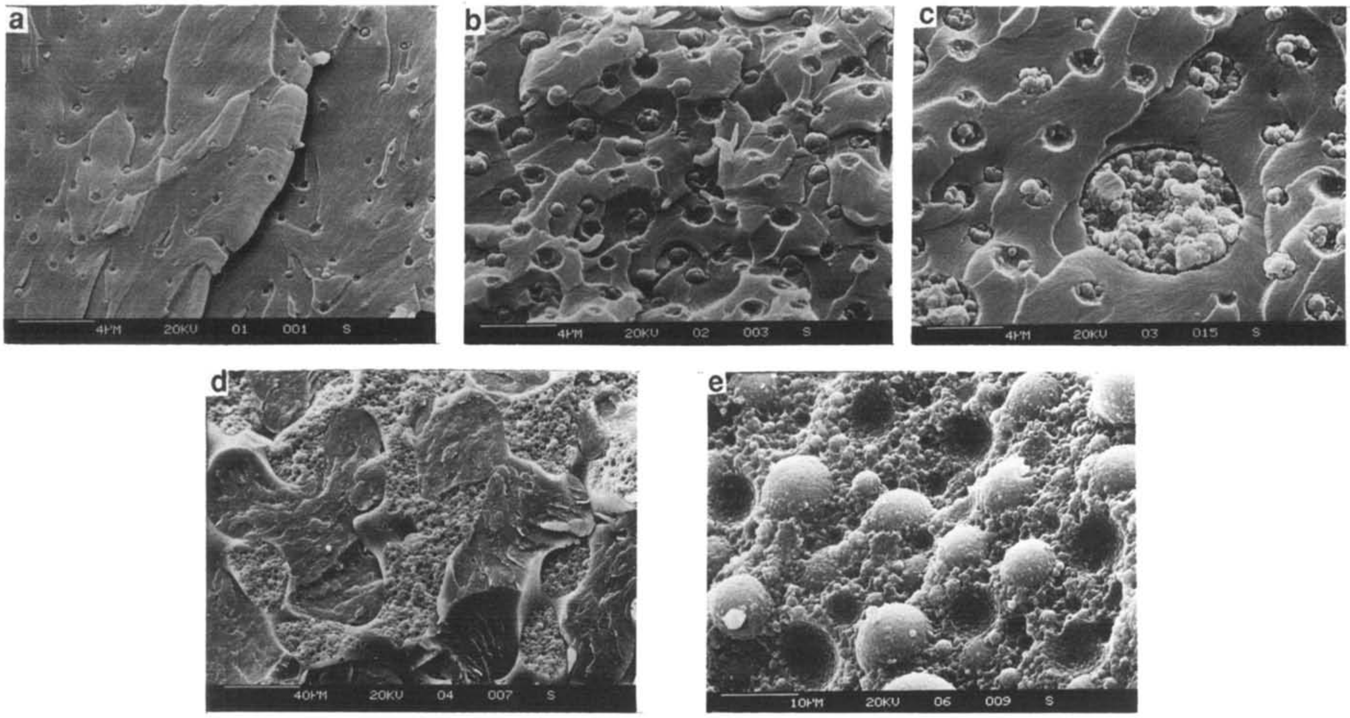

Figure 2 Scanning electron micrographs of 23°C fracture surfaces of blends containing various concentrations of PVAc: (a) 1%, (b) 2%, (c) 3%, (d) 4% and (e) 6%

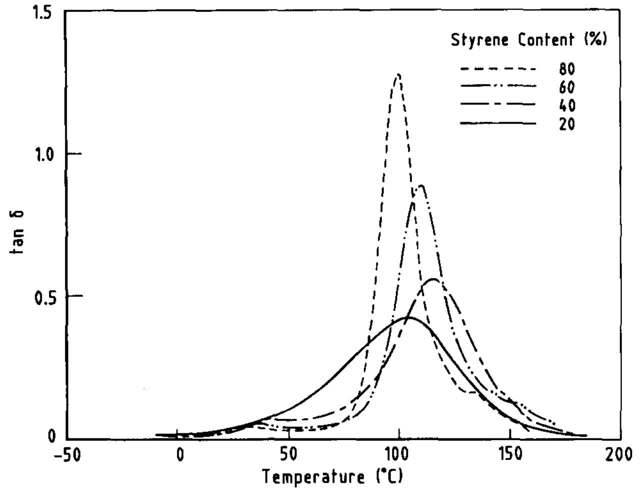

Figure 3 Variation of tan δ with temperature for blends containing 20%, 40%, 60% and 80% of styrene. Frequency 10 Hz

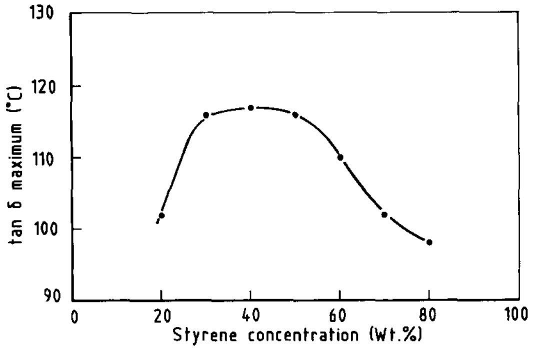

Figure 4 Effects of styrene content on T_g of polyester resins, as indicated by tan δ peaks from *Figure 3*

narrower and increase in height. Peak temperatures are plotted against styrene content in *Figure 4*: they show a systematic variation, rising from 103°C at a styrene/polyester (S/PE) ratio of 20/73, to a maximum of 115°C at S/PE = 40/53, before decreasing to 98°C at S/PE = 80/13.

In addition to the main peak, there are two secondary peaks. The lower of these, lying between 35 and 40°C, is clearly due to the glass transition of the PVAc component[3]. The upper peak, which appears as a shoulder on the main peak, lies in the temperature range 135–160°C, and is seen most clearly at the highest styrene levels. This suggests that it might be due to inhomogeneity in the styrene/polyester component when styrene is present in excess.

At a fixed styrene/polyester ratio of 40/60, increasing addition of PVAc produces a decrease in the height and area of the main resin peak near 100°C, and a corresponding rapid increase in the height and area of the PVAc peak near 40°C.

Modulus

Data obtained from 100 s creep tests at 20°C are presented in *Figures 5* and *6*. They show that Young's modulus is effectively independent of PVAc content over the range 0–10%, remaining close to 3.5 GPa despite the changes in morphology. Increases in styrene content in blends containing 6% PVAc caused an approximately linear decrease in modulus, from 3.6 to 2.8 GPa over the range of compositions studied.

Fracture resistance

Fracture data are shown in *Figures 7* and *8*. Values of G_{Ic} were calculated from K_{Ic} using the equation:

$$G_{\mathrm{Ic}} = (1 - \nu^2)K_{\mathrm{Ic}}^2/E$$

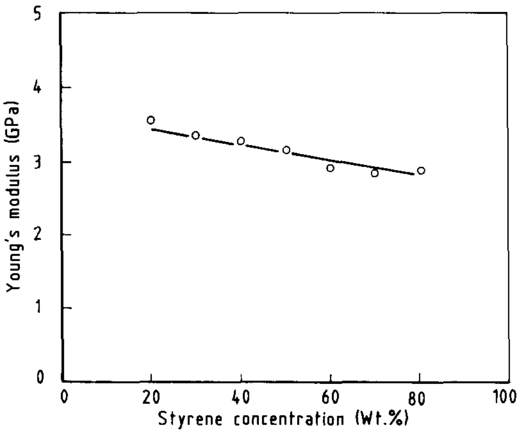

Figure 5 Relationship between Young's modulus and styrene content in blends containing 6% PVAc

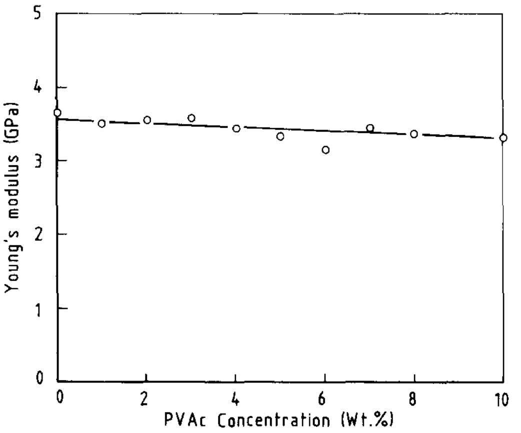

Figure 6 Relationship between Young's modulus and PVAc content in blends having a styrene/polyester ratio of 40/60

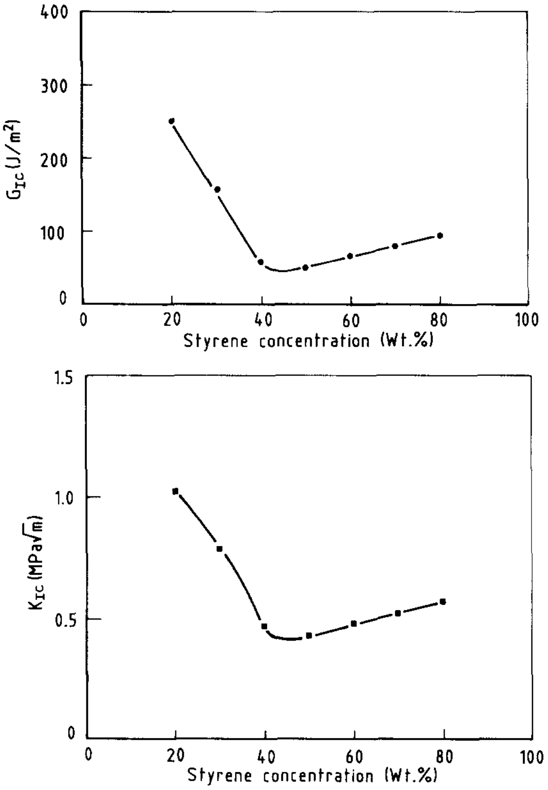

Figure 7 Relationship between fracture resistance and styrene content in blends containing 6% PVAc

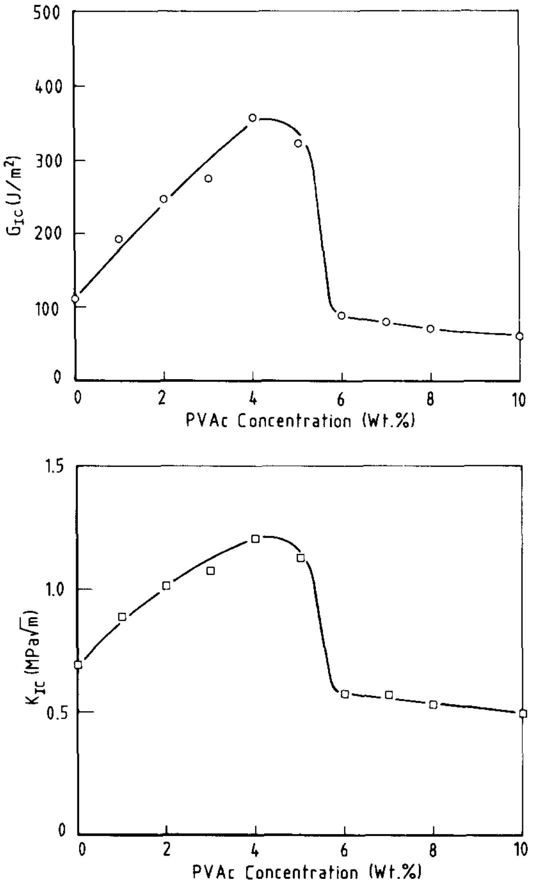

Figure 8 Relationship between fracture resistance and PVAc content in resins having a styrene/polyester ratio of 40/60

where ν and E are Poisson's ratio and Young's modulus obtained from creep tests. Because room-temperature values of Young's modulus do not vary strongly with composition, G_{Ic} is similar to K_{Ic} in its dependence upon styrene and PVAc concentrations.

Fracture resistance is high at low styrene levels, decreases to a minimum at 40–50% styrene, and then rises slowly. At a fixed S/PE ratio of 40/60, G_{Ic} and K_{Ic} increase approximately linearly with PVAc content, reaching a peak at 4% PVAc before falling sharply; between 6 and 10% PVAc, toughness values are lower in the blends than in the neat resin, and change little with composition.

DISCUSSION

The change from particulate to co-continuous morphology observed in the present study occurred at a PVAc concentration of approximately 5 wt%, whereas a previous paper from this laboratory reported a transition on addition of between 8% and 16% of PVAc modifier[2]. This difference in transition level is due to differences in molecular weight and chemical structure between the plain PVAc used in the present work and the commercial modifiers studied previously. Qualitatively, the changes in microstructure with composition are similar in the two cases. A similar change from particulate to co-continuous structure occurs on increasing the ratio of styrene to polyester in the blend.

The mechanism of phase separation cannot be deduced from an examination of final morphology. In view of the turbidity observed in some of the mixtures, it is possible that single-phase styrene solutions, containing both PVAc and resin, were not obtained in all cases, and that the co-continuous morphologies reported here resulted from coarsening of structures that were present at the beginning of the curing reaction. However, co-continuous structures can also be formed by spinodal decomposition[3], or by a nucleation and growth mechanism.

The dynamic mechanical data on blends containing various amounts of styrene show the effects of varying the degree of crosslinking in the resin. At an S/PE ratio of 20/73, corresponding to 0.9 moles per maleic group, the resin is insufficiently crosslinked, and its T_g is low in comparison with the blends containing 30, 40 and 50% styrene, all of which have tan δ peaks at 115°C. Another consequence of reduced crosslinking at $S/PE = 20/73$ is a broadening of the relaxation peak, which extends from 20 to 180°C. At the other end of the scale, styrene concentrations higher than 50% produce materials that are closer to polystyrene in their dynamic mechanical properties, with $T_g \approx 100$°C. These materials also show a small high-temperature peak, which is probably due to partial demixing of more tightly crosslinked resin molecules from the styrene-rich matrix.

At 20°C, the blends are below the T_g of PVAc. Despite the formation of co-continuous structure at low concentrations of PVAc, the 100 s creep modulus is essentially unaffected by the amount of modifier added, provided that the degree of crosslinking is kept constant. On the other hand, increasing the styrene/polyester ratio at fixed PVAc concentration causes a slow decrease in modulus.

The correlation between morphology and fracture resistance is the most striking feature of the results. Whilst the structure is particulate, with a dispersion of PVAc-based composite particles in a continuous resin matrix, the blends are tougher than plain polyester resin, and fracture resistance increases with PVAc concentration. In this respect, the PVAc behaves like a conventional toughening rubber, although it is below its observed T_g. Triaxial tensile stresses due to differential thermal contraction are known to shift the T_g of rubber particles downwards[4] by as much as 10 K, and a similar effect is to be expected in the triaxial tensile stress fields at the tips of sharp cracks. Detailed studies of the toughening mechanism have not yet been undertaken, but in view of the extent of crosslinking in the resin matrix, shear yielding in the resin is almost certainly the principal energy-dissipating process[5]. In the light of observations on toughened epoxy resins, yielding is probably facilitated by cavitation within the dispersed particles[6,7].

Quite different fracture behaviour is observed in blends that form co-continuous structures. As measured by G_{Ic}, energy to fracture is little more than half that absorbed by the plain polyester resin. It appears that the PVAc provides a low-energy pathway for fracture, and that energy absorption in the resin is therefore substantially reduced when the morphology becomes co-continuous.

This transition appears to provide the key to shrinkage control, which is exercised by commercial 'low-profile' modifiers in SMC and DMC formulations. The mechanism is the subject of a separate paper[8], in which it is shown that reduced shrinkage is the result of microcracking, caused by internal or external stresses acting on the weakened co-continuous resin/PVAc blend. Internal stresses arise in SMC and DMC because fibres and mineral filler particles resist shrinkage of the polyester during cure. Recommended levels of modifier for commercial polyester resin systems are relatively high, ensuring that a co-continuous structure is formed.

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